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Occurrence, sources and transport pathways of natural and anthropogenic hydrocarbons in deep-sea sediments of the Eastern Mediterranean Sea

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Abstract

Surface sediments collected from deep basins (22 stations, 1018–4087 m depth) of the Eastern Mediterranean Sea (EMS) were analyzed for aliphatic, triterpenoid and polycyclic aromatic hydrocarbons (PAHs) as tracers of natural and anthropogenic inputs. Concentrations of total aliphatic hydrocarbons (TAHC), *n*-alkanes (NA) and the Unresolved Complex Mixture (UCM) of aliphatic hydrocarbons ranged from 1.34 to 49.2 $\mu g\,g^{-1}$, 145 to 4810 $ng\,g^{-1}$ and 0.73 to 36.7 $\mu g\,g^{-1}$, respectively, while total PAHs ($TPAH_{25}$) concentrations ranged from 11.6 to 223 $ng\,g^{-1}$. Molecular profiles of aliphatic hydrocarbons and PAHs reflect the contribution of both natural (epicuticular plant waxes) and anthropogenic (degraded petroleum products, unburned fossil fuels and combustion of petroleum, grass, wood and coal) compounds in deep EMS sediments, with hydrocarbon mixtures displaying significant regional variability. Hydrocarbon concentrations correlated significantly with the Total Organic Carbon (TOC) content of sediments, indicating that organic carbon exerts an important control on their transport and fate in the study area, while strong sub-basin and mesoscale variability of water masses also impact their regional characteristics. Major findings of this study support that deep basins/canyons of the EMS could act as traps of both natural and anthropogenic hydrocarbons.

1 Introduction

Hydrocarbons are abundant components of both natural and anthropogenic organic material introduced in coastal and open sites of the world's oceans. They enter the marine environment through both atmospheric (dry/wet deposition, gas exchange across the air–water interface) and aquatic pathways (continental run-offs, direct discharges, off-shelf export), or are produced autochtonougly from marine organisms. Due to their hydrophobic nature hydrocarbons tend to associate with particles resulting in their transport and final accumulation in sediments (Bouloubassi et al., 2006, 2012;

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Castro-Jiménez et al., 2012; Dachs et al., 2002; Lipiatou et al., 1997; Parinos et al., 2012; Prahl and Carpenter, 1979).

Polycyclic aromatic hydrocarbons (PAHs) are included in lists of priority chemical pollutants by international environmental agencies (EEA, EPA), since certain homologues are highly carcinogenic and mutagenic, exhibiting tendency to bioaccumulate in aquatic organisms (Samanta et al., 2002 and references therein). Similarly, the Unresolved Complex Mixture (UCM), consisting of branched alicyclic hydrocarbons (Gough and Rowland, 1990; Killops and Al-Juboori, 1990), which is a commonly observed contaminant of marine sediments in which it can persist for decades (Reddy et al., 2002), has been proven as toxic to sediment-dwelling organisms (Scarlett et al., 2007).

Natural sources of hydrocarbons in the marine environment include terrestrial plant waxes, diagenetic transformation of biogenic precursors, marine phytoplankton and bacteria (Gogou et al., 2000). Major anthropogenic sources are industrial outfalls, petroleum processing/seepage and accidental oil spills, since hydrocarbons are main constitutes of petroleum, pyrolysis/combustion of organic material (e.g. biomass burning, incomplete combustion of fossil fuels) and several industrial processes (Countway et al., 2003; Dachs et al., 1997; Laflamme and Hites, 1978; Leister and Baker, 1994; Neff, 1979; Simoneit, 1984; Tolosa et al., 1996; Yunker et al., 2002).

The Eastern Mediterranean Sea (EMS), and especially its coastal area, is a region under intense anthropogenic pressure from increasing industrial and urban activities, resulting in pollutant discharges (EEA, 2006). Being an important geographical region for merchant shipping and oil transportation, the EMS receives substantial amounts of petroleum discharges, mainly along shipping routes (UNEP, 2010). Atmospheric deposition is also an important route for the introduction of hydrocarbons across the EMS (Castro-Jiménez et al., 2012; Gogou et al., 1996; Grimalt et al., 1988; Tsapakis 2003; Tsapakis and Stefanou, 2005), which also receives significant Saharan dust inputs (Jickells et al., 2005), during dust storm events, that contain both natural and anthropogenic hydrocarbons as recently reported (Ladji et al., 2010).

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Aliphatic hydrocarbons and PAH burden of surficial sediments in the EMS has been studied over the past twenty five years in coastal or shallow basin sites, namely the Aegean Sea, Cretan Sea (Southern Aegean sea), northeastern Mediterranean coast, southern Italy, Egypt coast and Adriatic Sea (Aboul-Kassim and Simoneit, 1995; Alebic-Juretic, 2011; Annicchiarico et al., 2011; Barakat et al., 2011; Botsou and Hatzianestis, 2012; Cardellicchio et al., 2007; Gogou et al., 2000; Gonul and Kucuksezgin, 2012; Guzzella and De Paolis, 1994; Hatzianestis et al., 2001; Kucuksezgin et al., 2012; Marcomini et al., 1986; Nemr et al., 2007; Sklivagou et al., 2008; Yilmaz et al., 1998; Youssif, 2002). However, there is a lack of data regarding hydrocarbons occurrence in deep basins of the EMS. Unlike coastal settings, deep-sea sediments reflect averaged deposition patterns and concentrations of natural and anthropogenic material of wider timeframes, due to the low sediment accumulation rates. In this study we focus on aliphatic, triterpenoid and polycyclic aromatic compounds as tracers of natural and anthropogenic inputs, reporting the first data set being addressed for surface sediments in deep EMS basins (22 stations, 1018–4087 m depth). Our main goal was to infer conclusions regarding their occurrence, major sources and transport pathways and to examine the role of deep EMS basins as repositories of hydrocarbons.

2 Oceanographic setting

The EMS is a semi-enclosed basin that connects with the Western Mediterranean Sea through the straits of Sicily. It includes four major sub-basins, the Ionian and Levantine basins, the Adriatic Sea and the Aegean Sea (Malanotte – Rizzoli et al., 1988; Robinson et al., 1992, 2001). It has a complex circulation pattern with water masses distribution being influenced by both large-scale and mesoscale variability (Malanotte-Rizzoli et al., 1997; Millot, 2005). As a concentration basin, it is characterized by an antiestuarine circulation that transforms surface Atlantic Waters (AW), entering through the strait of Sicily at the upper 100–150 m of the water column, into Levantine Intermediate Waters (LIW) in the eastern part of the region (Rhodes gyre). LIW leave the basin as

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a westward current through the Sicily strait at depths between 200 m and 500 m. The Aegean Sea occasionally contributes saline intermediate water masses to the EMS (Cretan Intermediate Water – CIW) with characteristics very close to those of LIW. Strong mesoscale variability, creating permanent and transient eddies and gyres, enhances exchanges between the continental shelf waters and slope waters (Danovaro et al., 2010).

Deep water layers of the EMS originate mainly in the Adriatic Sea and are exported by means of bottom-arrested currents toward the abyssal layers of the Ionian basin, flowing in an eastward path all the way towards the eastern Levantine basin. The Aegean Sea can also contribute in deep water formation and may even become more effective than the Adriatic as a deep water source for the EMS, as in the case of the Eastern Mediterranean Transient (EMT) during the early '90s (Civitarese et al., 2010; Roether et al., 1996; Theoharis et al., 1999).

Mean sedimentation rates in the EMS basins are low and generally do not exceed 5 cm kyr^{-1} mainly due to the oligotrophic character of the area (Garcia-Orellana et al., 2009).

3 Materials and methods

3.1 Sampling

Surface sediments were collected with a multicorer at twenty two stations in deep basins (1018–4087 m depth) of the Ionian Sea, Cretan Sea (southern Aegean Sea) and Levantine Sea, during four oceanographic cruises conducted between January 2007 and June 2012 (Fig. 1; Table 1). January 2007 samples were collected during the M71 Leg. 3 cruise of the R/V *Meteor* (University of Hamburg, Germany). May 2010, 2011 and June 2012 samples were collected during cruises of the R/V *Aegaeo* (HCMR, Greece). The undisturbed top centimeter (1 cm) of each core was recovered, wrapped in aluminum foil and stored at −20 °C till analysis.

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3.2 Methods

Freeze-dried sediments were spiked with a mixture of internal standards ([$^2H_{50}$]tetracosane, [$^2H_{10}$]phenanthrene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]perylene and [$^2H_{12}$]benzo[*ghi*]perylene) and solvent extracted three times by sonification with a dichloromethane : methanol mixture (4 : 1 v/v). Combined extracts were fractionated on silica column, applying a modified protocol after Gogou et al. (1998). Aliphatic hydrocarbons were eluted with 6 mL *n*-hexane and PAHs with 10 mL *n*-hexane/toluene (9 : 1, v/v). Both fractions were concentrated by vacuum rotary evaporation, transferred to a 1.5 mL amber vial and finally evaporated under a gentle nitrogen stream.

Instrumental analysis was carried out by Gas Chromatography–Mass Spectrometry (GC–MS) on an Agilent 7890 GC, equipped with an HP-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 µm phase film), coupled to an Agilent 5975C MSD. For the analysis of aliphatic hydrocarbons the MSD operated in full scan mode and the GC oven temperature was initially held at 60 °C for 2 min, brought to 80 °C at a rate of 25 °C min^{-1}, then to 300 °C at a rate of 5 °C min^{-1} and finally held at 300 °C for 35 min. PAHs were analyzed using a selected ion monitoring (SIM) acquisition program. The oven temperature program was the same as in the case of aliphatic hydrocarbons but with a 300 °C final isothermal of 6 min. Helium was used as carrier gas at a flow of 1.1 mL min^{-1}.

Standard solutions of the targeted compounds, purchased from Dr. Ehrenstorfer GmbH, were spiked with the internal standards and run on each injection set in order to derive relative response factors (RRFs) of the analytes. The precision of the analytical method used for PAHs was evaluated by analyzing the National Institute of Standards (NIST) standard reference sediment SRM 1941a (Organics in Marine Sediment). The determined values ranged between 93 and 106 % of the certified values while in terms of repeatability the relative standard deviation was below 5 %. Procedural blanks processed were found to be free of contamination.

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Spatial distributions of concentrations and characteristic parameters of aliphatic and polycyclic aromatic hydrocarbons were visualized using Ocean Data View – ODV (Schlitzer, 2011).

4 Results

4.1 Molecular profile of hydrocarbons

C_{12} to C_{42} *n*-alkanes (NA) were the main constituents of the resolved aliphatic compounds, representing on average 56 % of their total sum. Their molecular profile (Fig. 2a) was dominated by long chain homologues ($C_n \geq 24$) maximizing at C_{31} with an elevated odd/even carbon preference ($CPI_{24-35} > 1.9$, 4.3 on average; Table 2). NA with $C_n > 35$ constituted a large fraction (> 30 %) at some stations, while NA with $C_n \leq 23$ were mostly minor constituents and did not exhibit any odd/even carbon preference ($CPI_{14-23} \sim 1$). A UCM, present as a unimodal hump centered at C_{30}, was the major component of total aliphatic hydrocarbons (69 % on average).

25 PAHs comprising parent (unsubstitued) compounds with 2–6 aromatic rings and alkyl-substituted homologues were determined. A typical molecular profile of PAHs is presented in Fig. 2b. Phenanthrene and its methyl, di- and tri- methyl homologues dominated the low-MW PAH (≤ 3 aromatic rings). Their sum, referred to hereafter as ∑Phe, accounted for 23 ± 6 % of total PAHs. The high MW parent compounds (≥ 4 aromatic rings), which are of pyrolytic origin (Neff, 1979), were dominated by benzofluoranthenes, indeno[1,2,3-*cd*]pyrene and to a lesser degree chrysene. Their sum (referred to hereafter as ∑COMB), excluding perylene which may have natural sources (Venkatesan, 1988), represented 55 ± 8 % of total PAHs. Retene (methyl-1-isopropyl-7 phenanthene) was the major naturally-derived PAH determined in the study area (Ramdahl, 1983).

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4.2 Concentrations and spatial distribution of hydrocarbons

Concentrations of total aliphatic hydrocarbons (TAHC: sum of total resolved compounds and UCM), NA and UCM are presented in Table 2. TAHC and UCM concentrations ranged from 1.34 to 49.2 $\mu g\,g^{-1}$ and 0.73 to 36.7 $\mu g\,g^{-1}$, respectively, while NA concentrations ranged between 145 and 4810 $ng\,g^{-1}$. Their spatial distribution shows a generally increasing trend from Cretan Sea and Levantine Sea stations towards the deep stations of Ionian Sea (Fig. 3a–c). Maximum concentrations are found at station H03 while minimum at station H12, both located in the Ionian Sea.

Table 3 summarizes concentrations of PAHs in surface sediments of the study area. $TPAH_{25}$ refers to the total sum of compounds monitored while $\sum PAH_{13}$ refers to the sum of 13 parent compounds mainly considered in marine pollution studies, i.e. Fl, Phe, Anth, Flth, Pyr, BaA, Chry, BFlths, BeP, BaP, IndP, BgP and DBA (for abbreviations of PAH compounds see Fig. 2b). $TPAH_{25}$ and $\sum PAH_{13}$ concentrations ranged from 11.6 to 223 $ng\,g^{-1}$ and from 5.90 to 130 $ng\,g^{-1}$, respectively. The concentrations of $\sum$COMB ranged from 5.08 to 118 $ng\,g^{-1}$ while $\sum$Phe ranged between 2.74 and 38.3 $ng\,g^{-1}$. The spatial distribution of $TPAH_{25}$, $\sum$Phe and $\sum$COMB concentrations is presented in Fig. 3d–f. Highest $TPAH_{25}$, $\sum$COMB and $\sum$Phe concentrations were recorded at station H05, while lowest ones were found at station H12, both located in the Ionian Sea. The spatial distribution of $TPAH_{25}$ (Fig. 3d) is similar to the one observed for TAHC (Fig. 3a).

5 Discussion

5.1 Hydrocarbons levels

Table 4 summarizes concentrations of aliphatic and polycyclic aromatic hydrocarbons in the study area and data reported in deep-sea sediments of the Mediterranean Sea and other open sites of the world ocean. TAHC concentrations in the study area are

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slightly higher than those reported in the Cretan Sea (Gogou et al., 2000) and comparable to those reported in the Black Sea (Wakeham et al., 1996). As for UCM and NA, concentrations reported in this study are higher than those reported for the open Western Mediterranean Sea (Tolosa et al., 1996) and Cretan Sea (Gogou et al., 2000), but lower than those reported in the Arctic Ocean (Yunker et al., 2011). Total PAH concentrations are comparable to those reported for deep-sea settings such as Cretan Sea (Gogou et al., 2000), central Pacific Ocean (Ohkouchi et al., 1999) and South China Sea (Liu et al., 2012; Yang et al., 2000), while are considerably lower from those recorded in other deep oceanic sites: the Black Sea (Wakeham et al., 1996), the Western Mediterranean Sea (Lipiatou and Saliot, 1991; Tolosa et al., 1996), the Atlantic Ocean (OSPAR QRS, 2000) and the Arctic Ocean (Yunker et al., 2011).

5.2 Sources of natural and anthropogenic hydrocarbons

5.2.1 Natural sources

The dominance of C_{25} to C_{35} *n*-alkanes (Fig. 2a) with an elevated odd/even carbon preference shows the importance of natural terrestrial inputs, derived from epicuticular plant waxes (Eglinton and Hamilton, 1967), throughout the study area. The sum of major terrestrial *n*-alkanes (C_{27}, C_{29}, C_{31} and C_{33}), referred to hereafter as Ter.NA, averaged 50 % of total NA (Table 2).

The low abundance of C_{15}, C_{17} and C_{19} *n*-alkanes (< 5 % of NA) reflects a minor contribution from marine sources. This is consistent with both the ultra-oligotrophic character of the Eastern Mediterranean Sea (Krom et al., 2003) and the preferential preservation of terrestrial over planktonic hydrocarbons in the marine environment (Prahl and Carpenter, 1984). Also, bacterial sources, evidenced by the presence of hopenes (hop-17(21)-ene, hop-13(18)-ene and 17β(H)-hop-22(29)-ene; Fig. 4) are also of minor importance.

Among PAHs, the presence of retene reflects inputs from terrestrial plants, mainly conifers (Wakeham et al., 1980) or inputs related to pinewood combustion (Ramdahl,

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1983). Retene represented less that 4 % of $TPAH_{25}$ in all stations, except station H05 in which accounted for ~ 18 % of total PAHs (see below Sect. 5.3).

5.2.2 Anthropogenic sources

The elevated relative abundance of UCM compared to the total resolved aliphatic hydrocarbons (TRes) (UCM/TRes = 1.6–5.7; Table 2) is a positive indication of contribution from degraded petroleum products (Brassell and Eglinton, 1980; Farrington and Quinn, 1973). Consistently, a series of C_{29}–C_{35} 17α(H),21β(H)-hopanes were identified in all samples (Fig. 4). The extended, C_{31}–C_{35}, homologues were present as pairs of the C_{22} diastereoisomers (22S and 22R), with a 22S/22S + 22R ratio close to 0.6, typical for petrogenic hydrocarbons (Mackenzie, 1984). At some stations, low-MW *n*-alkanes ($C_n \leq 23$) without odd/even carbon preference likely derive from fossil inputs (light diesel), although they may also represent reworked algal material (Saliot, 1981; Wang et al., 1999), while large amounts of *n*-alkanes with $C_n > 35$ point to enhanced contribution of heavy fuel oil residuals (Brooks et al., 1954; Hsieh et al., 2000).

Among PAHs, the dominance of alkylated phenanthrenes in the low-MW PAH and the high abundance of parent PAH with ≥ 4 aromatic rings (Fig. 2b), reflect an admixture of unburned fossil sources (petroleum) and combustion/pyrolysis of fossil fuels (LaFlamme and Hites, 1978; Sporstol et al., 1983; Wakeham et al., 1980). Source specific diagnostic ratios have been used in order to further assess PAH sources (Yunker et al., 2002). The Flth/(Flth + Pyr) and IndP/(IndP + BgP) ratios exhibit values > 0.50, averaging 0.60 ± 0.04 and 0.56 ± 0.02 respectively, indicating grass, wood and coal combustion as primary sources for these PAHs. The BaA/(BaA + Chry) ratio ranged between 0.15–0.35 (average 0.26 ± 0.04), indicating an admixture of pyrolytic and fossil contributions. As for low-MW PAH compounds, the $C_0/(C_0 + C_1)$ Phe ratio ranged between 0.33–0.70 (average 0.51 ± 0.10) indicating a varying contribution of pyrolytic (ratio > 0.5) and petroleum (ratio < 0.5) phenanthrenes sources in the study area.

The ratio of total phenanthrenes (∑Phe), mostly derived from petrogenic inputs, and ∑COMB, representing pyrolytic PAH, (∑Phe/∑COMB, 0.22 to 0.87, average

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0.45 ± 0.19; Table 3), reflects dominant pyrolytic sources for PAH mixtures in the study area (Bouloubassi and Saliot, 1993; Bouloubassi et al., 2001; Gogou et al., 2000; Parinos et al., 2012).

5.3 Regional characteristics of hydrocarbons

Cluster analysis (joining clustering method) was used to group stations with similar *n*-alkanes or PAH profiles. Ward's method was used for amalgamation of clusters while distances between objects were measured as Euclidean distances.

Figure 5 presents the hierarchical diagram obtained from the cluster analysis of stations with regard to their *n*-alkanes profile, using the relative homologues concentrations for the total sum of NA as starting data, clustered station sites and characteristic GC chromatographs for each returning cluster. Stations are clustered into three main groups. Cluster I stations (RED2.1, RED4, RED5, H04 and H07) are characterized by high abundances of Ter.NA along with low-MW homologues ($C_n \leq 23$). Cluster II stations (RED8, RED1.1, IER01, H12, RED15.1, RED9, H01, RED13 and Rho02) are characterized by high abundances of Ter.NA and low concentrations of both low and higher ($C_n > 35$) molecular weight compounds. Stations in cluster III (RED3, RED3.1, RED7, H02, Her01, Her03, H05 and H03) are characterized by high abundances of Ter.NA along with significant presence of long chain homologues ($C_n > 35$).

Stations were also grouped using cluster analysis with regard to PAH profile characteristics (relative compounds concentrations for $TPAH_{25}$). Figure 6 presents the hierarchical diagram obtained from cluster analysis, clustered station sites and molecular profile for each returning cluster. Stations are also clustered into three main groups. Cluster I stations (RED2.1, RED3.1, RED3, RED4, RED5, RED7, H03, H07, H04, H01, IER01 and H12) are characterized by the elevated abundance of all alkylated homologues monitored within the phenanthrene, dibenzothiophene, pyrene and chrysene series, indicating enhanced contribution of petrogenic PAHs. Cluster II stations (RED8, RED1.1, RED13, RED9, RED15.1, H02, Her03, Her01 and Rho02) on the other hand displays maximum concentrations for parent phenanthrene, pyrene and chrysene and

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less than 0.1 % of $TPAH_{25}$ for dibenzothiophene and it's alkylated homologues, together with maximum values for high-MW parent compounds, indicating dominant pyrolytic PAH contribution. Cluster III corresponding only to station H05 is characterized by the highest concentration of retene, while the distribution of other compounds, e.g. low abundance of alkylated compounds and ∑COMB being > 50 % of $TPAH_{25}$, point to dominant pyrolytic sources.

5.3.1 Ionian Sea

The ∑Phe/∑COMB ratio shows an increasing trend from Aegean Sea to Sicily straits (stations H02, H03 and H04; Fig. 7a) in agreement with decreasing trend of $C_0/(C_0 + C_1)$ Phe ratio values for the same stations (Fig. 7b), indicating an increase in the relative contribution of fossil fuels from east to west. Consistently, stations H02 and H03 display relatively elevated contribution of heavy oil residuals as inferred by $C_n > 35$ *n*-alkanes (Fig. 5c), station H03 presents maximum UCM concentrations (Fig. 3b; Table 2) and station H04 is characterized by $C_n \leq 23$ *n*-alkanes (Fig. 5c). The Ionian sea stations H02, H03 and H04 are located close to the main shipping route from Greece to Italy, displaying high oil spill density, with maximum in the area around station H04 (Ferraro et al., 2009). Additionally, atmospheric inputs should also be considered as a major source of fossil compounds at stations located in the open Ionian Sea, since the abundance of long chain *n*-alkanes ($C_n > 35$) has been reported in rural aerosol molecular profiles of the EMS (Gogou et al., 1996), while Castro-Jiménez et al. (2012) also reported high diffusive deposition fluxes for Phe, DBT, C_1-Phe and C_1-DBT in the area.

Station H07, off the Gulf of Taranto in southern Italy, lies in an area subjected to strong anthropogenic pressure (Annicchiarico et al., 2011; Cardellicchio et al., 2007). Our hydrocarbon data show indeed strong fossil inputs, reflected in the abundance of short chain *n*-alkanes ($C_n \leq 23$), PAHs profile and in the high ∑Phe/∑COMB ratio values (Figs. 5c, 6c, 7a; Table 3). Station H12 in the eastern Ionian Sea is located along a main shipping route from Aegean Sea to Adriatic Sea characterized by high

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density of likely oil spills (Ferraro et al., 2009). However, this station displays minimum values for TAHC, UCM and $TPAH_{25}$ concentrations (Tables 2 and 3; Fig. 3) and low $\sum$Phe/$\sum$COMB ratio value (Table 3), indicating low pollutant load and pyrolytic PAH predominance. The low hydrocarbon content of this station is probably related to strong near bottom currents (Poulos et al., 1999) that favour resuspension and dispersal of sedimentary material.

The renewal time of the Ionian deep and bottom waters is approximately 58 yr (Schlitzer et al., 1991). Thus, the deep Ionian basin may act as a long term depository of hydrocarbons exported from the Adriatic Sea, since the latter is the main deep water source (see Sect. 2). Supportive to this higher concentrations of particle-associated PAHs are reported for near bottom rather than surface waters of the Otranto Straits (Parinos, unpublished data) while near bottom concentrations also display a decreasing trend moving from the Otranto Straits to the deep basins of the central Ionian Sea (stations H05 to H03 of this study).

5.3.2 Cretan Sea (southern Aegean) and western Cretan-Antikythera straits

For station RED7, maximum values for $\sum$Phe/$\sum$COMB ratio along with low $C_0/(C_0 + C_1)$ Phe ratio values (Table 3), abundance of long chain *n*-alkanes (Fig. 5c) and finally, PAHs profile (Fig. 6c), indicate enhanced fossil inputs. Stations RED3 and RED3.1 located in the western Cretan-Antikythera straits also display enhanced fossil inputs, in contrast with stations in neighboring regions (Ionian Sea and Levantine Sea) where $\sum$Phe/$\sum$COMB and $C_0/(C_0 + C_1)$ Phe ratio values indicate dominant pyrolytic sources (Fig. 7a, b).

Elevated concentrations for petrogenic PAHs ($\sum$Phe) have been reported in central Aegean Sea and Cretan Sea sediments (Hatzianestis and Sklivagou, 2001; Hatzianestis et al., personal communication). These data combined with our results (Fig. 8) evidence a decreasing southward trend for %$\sum$Phe from central Aegean Sea to Cretan Sea and western Cretan-Antikythera straits. This trend could be attributed to

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the circulation patterns of the Aegean Sea and the chemical characteristics of low-MW petrogenic PAHs.

The latter are less hydrophobic and occur mainly in the dissolved phase, thus they display longer residence time in the water column and could be transported at long distances. The general cyclonic circulation of the Aegean Sea and the net outflow, in the upper 400 m of depth, towards the EMS observed in the western Cretan straits (Kontoyiannis et al., 1999, 2005) likely contribute to the transfer of petrogenic hydrocarbons from central Aegean Sea towards the western Cretan straits. This transfer may be enhanced during periods of deep water formation in the Aegean Sea, when dense water outflows through the eastern and especially the western Cretan strait canyons (Lykousis et al., 2011). The western Cretan strait canyons (stations RED3.1 and RED7) may thus represent a significant sink of hydrocarbons (Tables 2 and 3), in agreement with earlier observations regarding the transfer and distributions of organic pollutants in deep canyon settings (Bouloubassi et al., 2012; Dachs et al., 1997; Fang et al., 2009; Liu et al., 2009; Salvadó et al., 2012).

5.3.3 Levantine Sea

The presence of long chain ($C_n > 35$) *n*-alkanes (Fig. 5c) at stations located in Herodotus basin (Her01 and Her03) supports the importance of atmospheric deposition in this area. Her01 and Her03 also display a dominant pyrolytic PAH burden, as shown by the low $\sum$Phe/$\sum$COMB values (Table 3) and PAHs profile (Fig. 6c). In contrast, at stations around Ierapetra deep (IER01, RED1.1 and RED15.1) the values of $\sum$Phe/$\sum$COMB and $C_0/(C_0 + C_1)$ Phe and PAHs profile (Table 3; Fig. 6c) reflect an elevated petrogenic PAH contribution. The presence of the well documented Ierapetra anticyclone (Larnicol et al., 2002; Taupier-Letage, 2008), a semi-permanent eddy, further acts to entrap water masses exiting the Cretan sea, increasing the residence time of hydrocarbons and enhancing their downward transfer.

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5.4 Drivers of hydrocarbon's distribution in deep-sea sediments of the Eastern Mediterranean Sea

In order to assess the main processes driving hydrocarbon distributions in the study area, correlation analysis was performed for aliphatic and polycyclic aromatic hydrocarbons concentrations and Total Organic Carbon (TOC) content of sediments.

TAHC, UCM, NA, Ter.NA, $TPAH_{25}$, ∑Phe and ∑COMB concentrations show significant correlation with TOC (Table 5), indicating that organic carbon exerts an important control on the distribution of both natural and anthropogenic hydrocarbons in the study area. This is in agreement with earlier observations in coastal and open sea marine sediments (Bouloubassi et al., 2012; Charlesworth et al., 2002; De Luca et al., 2004; Gogou et al., 2000; Mayer, 1993; Oros and Ross, 2004; Readman et al., 2002; Tsapakis et al., 2003; Witt et al., 1995; Yang et al., 2000) and is attributed to the high affinity of hydrophobic aliphatic and polycyclic aromatic hydrocarbons to organic matter.

Overall, the concentrations of aliphatic hydrocarbons correlate with the water column depth indicating that sediments in the deep EMS basins act as their repository (Table 5). The significant correlation of UCM/TRes ratio to depth ($r = 0.556$, $p = 0.007$), imply that the accumulation is stronger for chronic anthropogenic (petrogenic) pollutant burden rather than for natural, biogenic hydrocarbons.

Although $TPAH_{25}$, ∑Phe and ∑COMB concentrations correlate to organic carbon, they do not correlate with water column depth (Table 5). Also, as discussed in Sect. 4.3, aliphatic and polycyclic aromatic hydrocarbons display different maximum concentration points, i.e. station H03 for aliphatic hydrocarbons and H05 for PAHs. The above imply that although organic carbon exerts the main control on the distribution of both TAHC and $TPAH_{25}$ in the study area, an additional factor affects the dispersal of PAHs. Elemental (black) carbon and especially the partioning between natural organic carbon and combustion derived black carbon has been reported to exert the main control on PAHs regional distribution (Accardi-Dey and Gschwend, 2002, 2003). It is well documented that high-MW pyrolytic PAH show greater affinity to soot (black carbon)

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rather than organic carbon (Boehm and Farrington, 1984; Dachs and Eisenreich, 2000; Gustaffson et al., 1997), while low-MW PAH (mostly of fossil origin) as more soluble are more efficiently scavenged by organic rich particles e.g phytoplankton and fecal pellets (Dachs et al., 1996, 1997).

6 Conclusions

Aliphatic hydrocarbons and PAHs in surface deep-sea sediments of the Eastern Mediterranean Sea (EMS) occur at levels in the same order of magnitude as those found in deep-sea settings in the Western Mediterranean Sea and worldwide. Their distribution is characterised by an increasing trend moving from Cretan Sea (Southern Aegean Sea) and Levantine Sea towards the deep basins of the Ionian Sea. Their molecular profiles evidence contributions of both natural and anthropogenic inputs in the study area. The former derive from terrestrial vegetation while the latter are related to both intense maritime traffic and atmospheric inputs. The composition of hydrocarbon mixtures displays significant regional variability reflecting the relative importance of sources.

Concentrations of both aliphatic and polycyclic aromatic hydrocarbons exhibit significant correlations with organic carbon contents, indicating that the latter exerts a main control on the transport, fate and ultimate accumulation of both natural and anthropogenic chemical species in the deep basins of the EMS. Aliphatic hydrocarbon concentrations correlate with water column depth, emerging the role of deep EMS basins as repositories for these compounds, while the lack of correlation between PAH concentrations and depth imply that PAHs distribution is not controlled by organic carbon alone, but probably from the partioning between natural organic carbon and combustion derived elemental (black or soot) carbon.

Distribution of hydrocarbons in the study area is also driven by strong sub-basin and mesoscale variability of water masses that impact their regional characteristics. Our results imply a transport of more soluble petrogenic PAHs from the central Aegean Sea

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through the western Cretan-Antikythera straits to the western Cretan straits canyons, the latter acting as a sink of hydrocarbons. Further investigation is needed on the impact of organic pollutants to deep-sea biological communities.

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Table 1. Detailed location and characteristics of sampling sites.

Station	Location Lat. N	Long. E	Water depth (m)	Sampling date	TOC (%)[a]
RED2.1	33° 42.81′	26° 20.45′	2720	May 2010	0.37
RED3	35° 24.14′	23° 24.10′	2976	May 2010	0.37
RED3.1	35° 18.17′	23° 18.92′	3314	May 2010	0.58
RED4	35° 45.71′	25° 06.00′	1620	May 2010	0.42
RED5	35° 40.57′	25° 06.12′	1018	May 2010	0.39
RED7	34° 36.11′	24° 08.73′	3589	May 2011	0.51
RED8	36° 04.47′	25° 17.07′	1715	May 2011	0.33
RED9	36° 00.03′	23° 53.55′	1200	May 2011	0.40
RED1.1	34° 24.13′	26° 14.67′	3568	Jun 2012	0.54
RED15.1	34° 36.55′	25° 55.49′	2428	Jun 2012	0.62
RED13	34° 57.01′	25° 54.90′	1101	Jun 2012	0.46
H01	35° 45.00′	23° 00.00′	2117	Jan 2007	0.29
H02	35° 45.00′	21° 00.00′	3008	Jan 2007	0.45
H03	35° 45.00′	18° 30.00′	4087	Jan 2007	0.63
H04	35° 55.00′	16° 00.00′	3750	Jan 2007	0.65
H05	37° 30.00′	18° 30.00′	3154	Jan 2007	0.57
H07	39° 10.00′	17° 45.00′	1866	Jan 2007	1.15
H12	38° 50.00′	19° 45.00′	1450	Jan 2007	0.15
Her01	33° 55.44′	27° 44.45′	2680	Jan 2007	0.31
Her03	33° 40.00′	29° 00.00′	3090	Jan 2007	0.49
IER01	34° 26.54′	26° 11.51′	3626	Jan 2007	0.52
Rho02	35° 37.12′	27° 42.03′	1305	Jan 2007	0.47

[a] TOC values from Pedrosa-Pàmies et al. (2012).

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Table 2. Concentrations and characteristic parameters of aliphatic hydrocarbons determined in deep-sea sediments of the Eastern Mediterranean Sea.

Station	TAHC ($\mu g g^{-1}$)	UCM ($\mu g g^{-1}$)	NA ($ng g^{-1}$)	Ter. NA ($ng g^{-1}$)	CPI_{24-35}	UCM/TRes
RED2.1	37.5	24.8	4810	1800	1.78	3.2
RED3	16.2	10.8	1680	442	2.37	2.9
RED3.1	43.2	31.7	3820	1260	2.78	4.1
RED4	13.0	7.75	1790	819	4.25	2.3
RED5	11.6	6.41	1660	805	4.07	1.8
RED7	28.6	21.7	2410	938	3.42	4.9
RED8	7.32	5.32	681	414	5.84	4.0
RED9	6.84	5.11	586	400	6.67	4.5
RED1.1	15.5	11.3	1500	892	5.51	4.2
RED15.1	15.1	10.8	1530	772	4.71	4.0
RED13	8.47	5.66	1050	720	7.28	3.2
H01	3.23	1.71	550	374	6.18	1.8
H02	20.1	14.5	2160	800	3.07	4.2
H03	49.2	36.7	4670	1350	2.26	4.7
H04	24.2	18.6	2090	1100	3.64	5.3
H05	32.0	23.9	2930	1210	3.51	4.5
H07	15.7	12.5	997	467	3.64	5.7
H12	1.34	0.73	145	80.7	3.66	1.6
Her01	12.4	8.64	1460	603	3.86	3.7
Her03	20.0	14.5	2100	767	3.13	4.2
IER01	15.1	10.6	1800	1070	5.75	3.9
Rho02	8.06	5.00	1160	774	6.26	2.6

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Table 3. Concentrations and source-specific diagnostic ratios of polycyclic aromatic hydrocarbons (PAHs) determined in deep-sea sediments of the Eastern Mediterranean Sea.

Station	$TPAH_{25}$ ($ng\,g^{-1}$)	$TPAH_{13}$ ($ng\,g^{-1}$)	∑COMB ($ng\,g^{-1}$)	∑Phe ($ng\,g^{-1}$)	∑Phe/∑COMB	$C_0/(C_0+C_1)$ Phe	Flth/(Flth + Pyr)	BaA/(BaA + Chry)	IndP/(IndP+BgP)
RED2.1	59.7	36.4	31.0	17.4	0.56	0.43	0.53	0.27	0.58
RED3	51.4	32.0	28.0	13.2	0.47	0.42	0.56	0.22	0.59
RED3.1	109	63.2	54.2	33.3	0.61	0.39	0.58	0.26	0.58
RED4	52.0	28.9	24.4	18.3	0.75	0.38	0.52	0.28	0.61
RED5	50.0	34.5	30.5	11.4	0.37	0.46	0.55	0.29	0.59
RED7	114	50.8	42.6	37.1	0.87	0.39	0.63	0.24	0.55
RED8	40.2	27.2	24.3	8.01	0.33	0.56	0.59	0.28	0.57
RED9	25.5	18.6	17.2	4.34	0.25	0.50	0.60	0.25	0.57
RED1.1	39.6	27.8	24.5	7.43	0.30	0.62	0.60	0.28	0.56
RED15.1	32.0	24.1	22.3	4.91	0.22	0.57	0.60	0.26	0.59
RED13	39.1	25.4	22.0	9.12	0.41	0.52	0.58	0.25	0.51
H01	11.6	5.90	5.08	4.42	0.87	0.33	0.59	0.21	0.55
H02	41.2	30.7	27.6	7.46	0.27	0.63	0.58	0.26	0.58
H03	93.9	54.4	49.5	19.2	0.39	0.50	0.61	0.22	0.54
H04	113	60.4	55.1	24.3	0.44	0.46	0.58	0.27	0.51
H05	223	130	118	38.3	0.32	0.55	0.65	0.35	0.54
H07	118	70.4	61.2	31.7	0.52	0.51	0.59	0.28	0.54
H12	17.5	9.58	8.26	2.74	0.33	0.70	0.67	0.15	0.58
Her01	45.3	32.7	28.7	8.53	0.30	0.65	0.62	0.32	0.55
Her03	29.9	20.9	18.9	6.04	0.32	0.57	0.66	0.25	0.57
IER01	42.7	23.4	21.0	12.7	0.60	0.44	0.63	0.19	0.58
Rho02	50.0	36.2	31.5	10.0	0.32	0.63	0.64	0.24	0.54

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Table 4. Concentrations of aliphatic and polycyclic aromatic hydrocarbons in the study area and data reported for deep-sea sediments of the Mediterranean Sea and other open sites of the world ocean.

Location	Depth (m)	Sediment Layer	TPAH ($ng\,g^{-1}$)	TAHC ($\mu g\,g^{-1}$)	UCM ($\mu g\,g^{-1}$)	NA ($ng\,g^{-1}$)	Reference
Eastern Mediterranean Sea	1101–4087	1 cm	11.6–213 ($\sum PAH_{25}$)	1.34–49.2	0.73–36.7	145–4810	This study
Black Sea	1500–2210	1 or 2 cm	320–1250 ($\sum PAH_{24}$)	< 22[a]			Wakeham et al. (1996)
Cretan Sea (Southern Aegean Sea)	700–1570	1 cm	14.7–128 ($\sum PAH_{24}$)	0.59–3.02	0.34–2.56	80–497	Gogou et al. (2000)
Central Pacific ocean	2505–5906	2 cm	0.81–60.6 ($\sum PAH_{14}$)				Ohkouchi et al. (1999)
South China Sea	1045–2432	2 cm	125–199 ($\sum PAH_{10}$)				Yang et al. (2000)
South China Sea	1050–2456	5 cm	40–109 ($\sum PAH_{18}$)				Liu et al. (2012)
Western Mediterranean Sea	750–2200	1 cm	325–1437 ($\sum PAH_{31}$)				Lipiatou and Saliot (1991)
Northwestern Mediterranean Sea	1790–2700	1 cm	100–500 ($\sum PAH_{22}$)		1–1.7	1000–1700	Tolosa et al. (1996)
Cap Ferret Canyon (Atlantic ocean)	615–1040	n.a	615–1040 (n.a.)				OSPAR, QRS (2000)
Arctic Ocean	2265–4230	1 cm	113–2504($\sum PAH_{29}$)			1760–12400	Yunker et al. (2011)

n.a: not available.
[a] all stations except Danube estuary (station 4T).

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Table 5. Statistically significant correlations for aliphatic and polycyclic aromatic hydrocarbon concentrations, TOC content and water column depth in the study area.

			TAHC	UCM	NA	Ter.NA	$TPAH_{25}$	∑COMB	∑Phe
(n = 22)									
	TOC	Pearson Correlation	0.625**	0.652**	0.525*	0.634**	0.544*	0.548*	0.514*
		Significance (2-tailed)	0.002	0.001	0.015	0.002	0.011	0.010	0.017
	Depth	Pearson Correlation	0.706**	0.730**	0.622**	0.565**			
		Significance (2-tailed)	< 0.0005	< 0.0005	0.002	0.006			
	TAHC	Pearson Correlation	1	0.995**	0.955**	0.834**	0.617**	0.587**	0.654**
		Significance (2-tailed)		< 0.0005	< 0.0005	< 0.0005	0.002	0.004	0.001
	$TPAH_{25}$	Pearson Correlation	0.617**	0.645**	0.478*	0.476*	1	0.981**	0.909**
		Significance (2-tailed)	0.002	0.001	0.024	0.025		< 0.0005	< 0.0005

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

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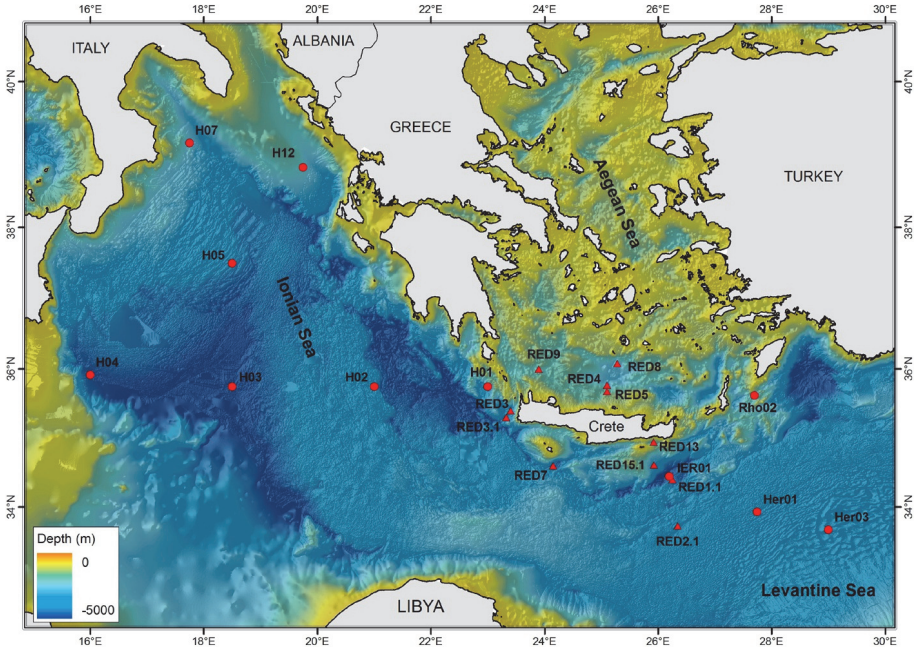

Fig. 1. Study area and location of sampling sites across the Eastern Mediterranean Sea. Sites presented as circles represent sediments collected during January 2007 cruise, while sites presented as triangles represent sediments collected during May 2010, 2011 and July 2012 cruises (Table 1). The map was produced using GEBCO Digital Atlas (IOC, IHO and BODC, 2003).

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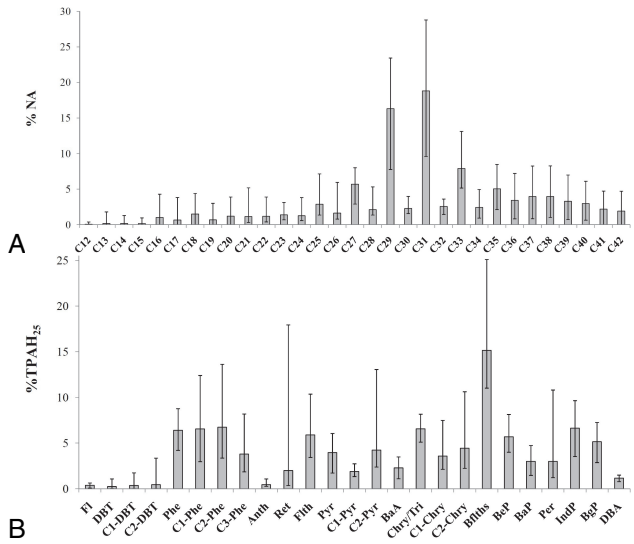

Fig. 2. Molecular profile for *n*-alkanes **(A)** and PAHs **(B)** in deep-sea sediments collected across the Eastern Mediterranean Sea. Individual compound abundances are normalized as percentage of the total sum of NA or PAHs ($TPAH_{25}$) respectively and presented along with min-max deviation lines. NA homologues are assigned with their carbon atoms number. PAH abbreviations: Fluorene (Fl); dibenzothiophene (DBT); methyl-dibenzothiophenes (C_1-DBT); dimethyl-dibenzothiophenes (C_2-DBT); phenanthrene (Phe); methyl-phenanthrenes (C_1-Phe); dimethyl-phenanthrenes (C_2-Phe); trimethyl-phenanthrenes (C_3-Phe); anthracene (Anth); fluoranthene (Flth); pyrene (Pyr); methyl-pyrenes (C_1-Pyr); dimethyl-pyrenes (C_2-Pyr); retene (Ret); benzo[*a*]anthracene (BaA); chrysene/triphenylene (Chry/Tri); methyl-chrysenes (C_1-Chry); dimethyl-chrysenes (C_2-Chry); benzo[*b*/*j*/*k*]fluoranthene (BFlths); benzo[*e*]pyrene (BeP); benzo[*a*]pyrene (BaP); perylene (Per); indeno[1,2,3-*cd*]pyrene (IndP); benzo[*ghi*]perylene (BgP) and dibenzo[*a*,*h*]anthracene (DBA).

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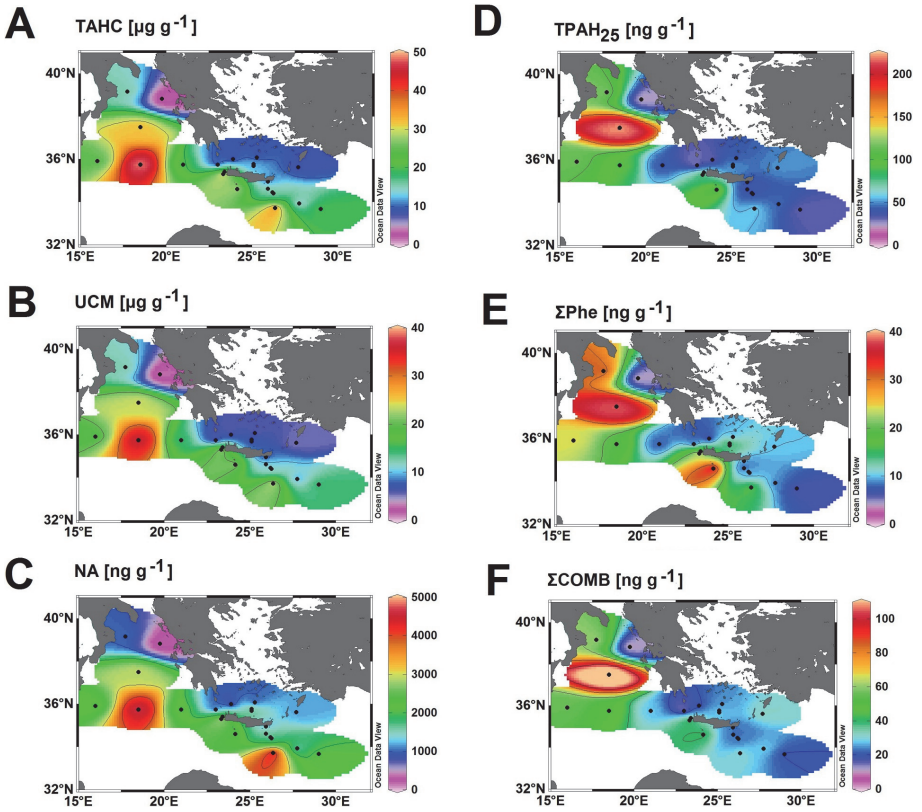

Fig. 3. Spatial distribution of aliphatic and polycyclic aromatic hydrocarbons concentrations in deep-sea sediments across the Eastern Mediterranean Sea.

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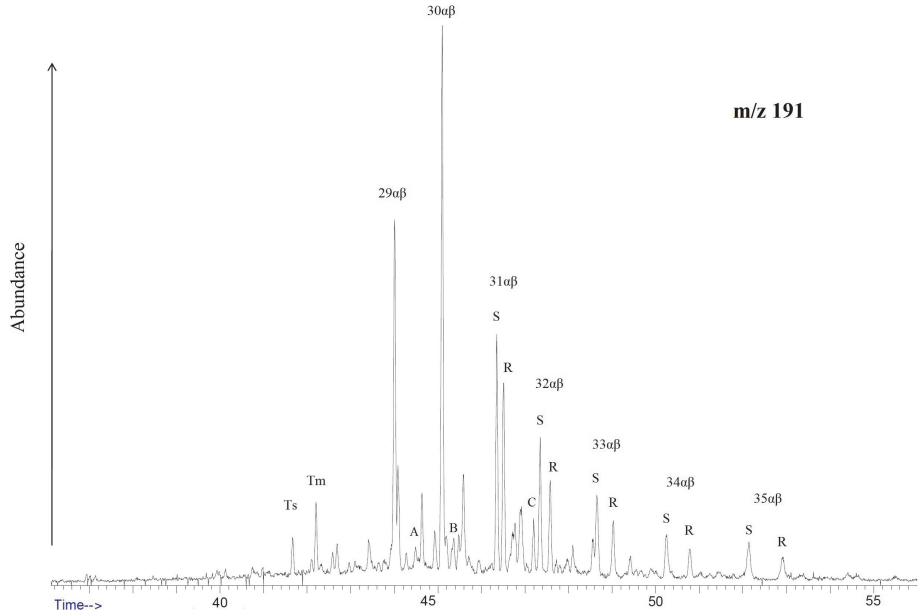

Fig. 4. Characteristic ion fragmentogram (*m/z* 191). Hopanes: Ts: 18α(H)-22, 29,30-trisnorneohopane, Tm: 17α(H)-22,29,30-trisnorhopane. 29$\alpha\beta$: 17α(H),21β(H)-30-norhopane. 30$\alpha\beta$: 17α(H), 21β(H)-hopane. 31$\alpha\beta$: 17α(H), 21β(H)-homohopanes (22S and 22R). 32$\alpha\beta$: 17α(H),21β(H)-bishomohopane (22S and 22R). 33$\alpha\beta$: 17α(H),21β(H)-trishomohopane (22S and 22R). 34$\alpha\beta$: 17α(H),21β(H)-tetrakishomohopane (22S and 22R). 35$\alpha\beta$: 17α(H),21β(H)-pentakishomohopane (22S and 22R). Hopenes: A: hop-17(21)-ene. B: hop-13(18)-ene. C: 17β(H)-hop-22(29)-ene (Diploptene).

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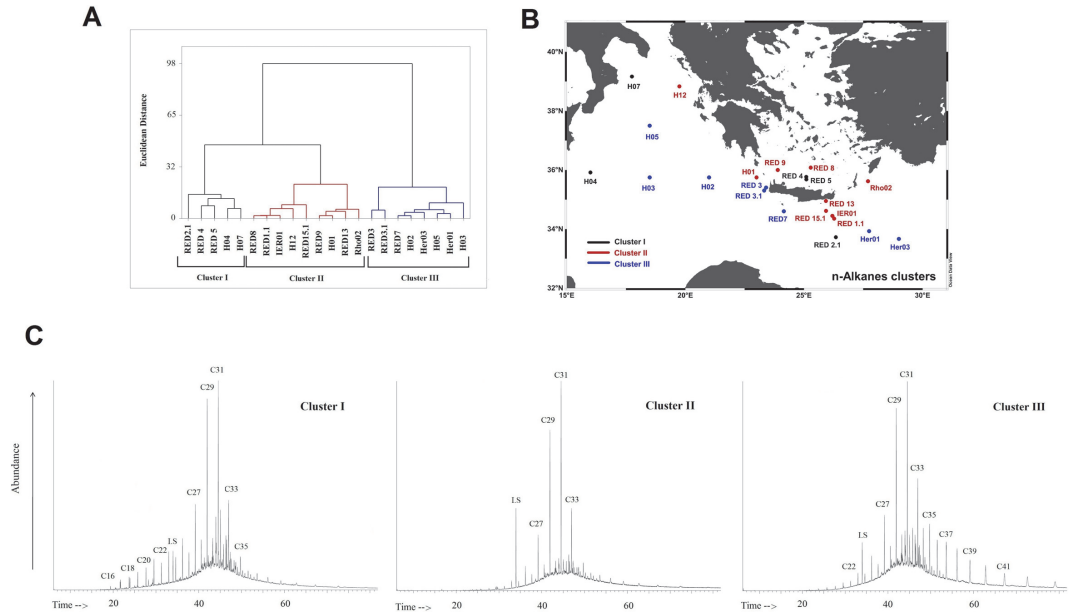

Fig. 5. Hierarchical diagram obtained from cluster analysis of all stations with regard to *n*-alkanes profile **(A)**, clustered station sites **(B)** and characteristic GC-MS chromatographs for each returning cluster **(C)**. Cluster I: Station H03, Cluster II: Station RED9 and Cluster III: Station Her03. I.S: Internal Standard.

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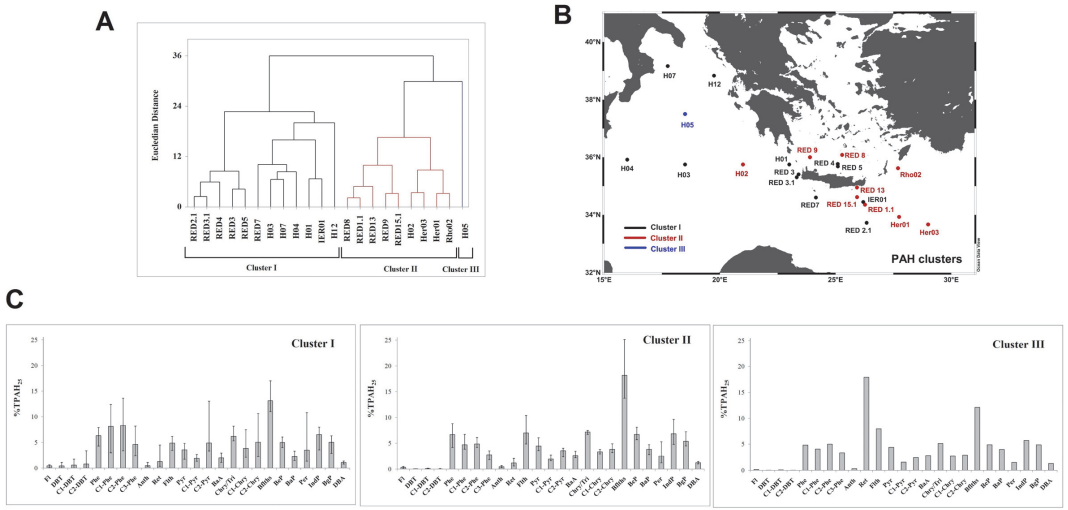

Fig. 6. Hierarchical diagram obtained from cluster analysis of all stations with regard to PAH profile characteristics **(A)**, clustered station sites **(B)** and molecular profile for each returning cluster **(C)**. Individual compound abundances are normalized as percentage of $TPAH_{25}$ and presented along with min-max deviation lines.

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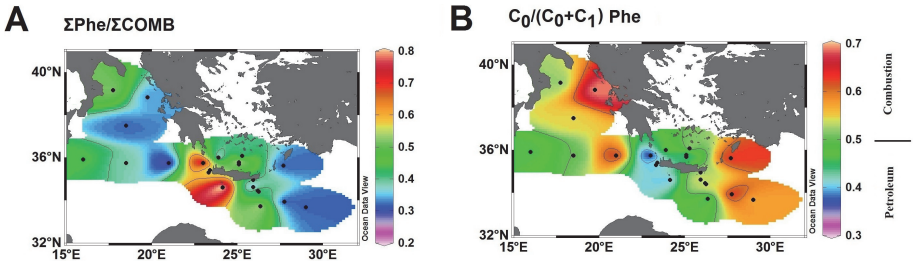

Fig. 7. Spatial distribution of ∑Phe/∑COMB **(A)** and $C_0/(C_0 + C_1)$ Phe **(B)** ratios in the study area.

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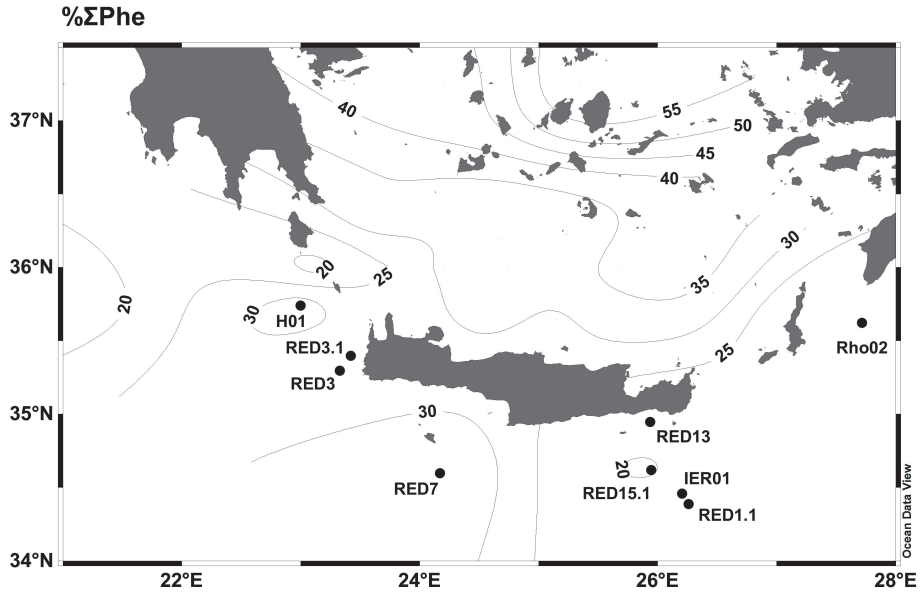

Fig. 8. Spatial distribution of %∑Phe in Cretan Sea (southern Aegean Sea) and western Cretan-Antikythera straits surface sediments. Data for Cretan Sea sediments are a combination of data reported in this study and data reported (stations not shown) by Hatzianestis and Sklivagou (2001).

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